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ELECTROLYTIC PRODUCTION OF LEAD CHROMATES

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4 Claims. (Cl. 204—89)

This invention relates to the production of lead chromates and has for its principal object the provision of an improved electrolytic method for manufacturing lead chromate products. This application is a continuation in part of my co-pending application, Serial No. 134,520, filed April 2, 1937.

In my above-mentioned application I have described an improved process for the electrolytic manufacture of metal chromate products, particularly lead chromates, by means of which it is possible to control the chemical composition and the physical properties of the chromate products formed. The chromate products are formed electrolytically by passing an electric current from a soluble lead anode through an anolyte comprising a solution of a substance capable of serving during electrolysis as a solvent for the lead of the anode, a diaphragm, and a catholyte containing chromate ions to a cathode. In my aforementioned application the use of an anolyte comprising an aqueous solution of sodium acetate or sodium chlorate is referred to. I have now found that improved results may be secured in carrying out this process by employing as the anolyte a solution of a substance capable of yielding nitrate ions during electrolysis. Preferably an aqueous solution having an alkali metal nitrate dissolved therein is employed as the anolyte. Sodium nitrate, potassium nitrate, or ammonium nitrate may be employed as the alkali metal nitrate used in making up the anolyte, but in general the use of sodium nitrate is most economical and convenient and is preferred.

A complete process embodying the present invention may be carried out in a bifluid electrolytic cell comprising a lead anode immersed in an anolyte containing a substance capable of yielding nitrate ions during progress of the electrolytic operation. An aqueous solution of an alkali metal nitrate, advantageously sodium nitrate, preferably is employed as the anolyte. The anolyte is separated from a catholyte in the cell by a permeable diaphragm. The catholyte comprises a solution containing a substance capable of yielding chromate ions during the course of the electrolytic operation. An aqueous solution containing sodium chromate or sodium dichromate is in general preferred for use as the catholyte. A cathode capable of conducting electric current is immersed in the catholyte.

The complete apparatus employed preferably includes means for circulating anolyte and catholyte solution through the anolyte and catholyte compartments in the cell, and to and from anolyte and catholyte storage compartments outside the cell. Means are included in the anolyte circulation system outside the cell for separating the chromate product formed in the anolyte. Means are provided for adding a substance capable of yielding chromate ions to the catholyte, preferably during circulation of the catholyte outside the cell.

The production of lead chromate products in the cell described is accomplished by passing an electric current through the cell between the lead anode and the cathode. The lead chromate product is formed in the anolyte during the course of the electrolysis and is separated from the anolyte, preferably during circulation of the anolyte outside the cell.

Lead chromate products made in accordance with the present invention employing a nitrate anolyte in general are superior to lead chromate products produced by heretofore known methods. For example, lead chromate pigments produced electrolytically with the use of a nitrate anolyte generally are of finer and more uniform particle size, exhibit a greater degree of color or tint retention, are more resistant to color changes induced by exposure of the pigment to light, and give cleaner and clearer tints and are less subject to chalkiness when employed as pigments in paint or similar products.

In addition to yielding a superior product, the improved method of the invention results in substantial operating economies. For example, a process employing an acetate anolyte operates, at a temperature of about 25° C. with a cell voltage of about 4.3, whereas the new process involving the use of a nitrate anolyte operates at the same temperature with a cell voltage of about 3.5, other factors remaining the same. In the case of a cell unit operating with a total current consumption of 4,000 amperes (a typical current consumption for a commercial cell utilized in the electrolytic production of lead chromate), this reduced voltage results in a power saving of about 3,200 watts. Even in operating at electrically more efficient higher temperatures, the nitrate process of the invention leads to substantial power savings. At about 50° C., for example, the cell voltage will amount to about 2.6 volts when using an acetate anolyte, but will amount only to about 2.3 volts when employing a nitrate anolyte, other factors remaining the same. This reduced voltage results in a power saving of about 1,200 watts per cell operating at 4,000 amperes.

In addition to the foregoing advantages, the

use of nitrate anolytes leads to further economies due to the fact that nitrate salts are less expensive and more readily procured and handled than the corresponding acetate or chlorate salts, which heretofore have been employed in electrolytic manufacture of lead chromates.

In carrying out a process for the production of lead chromate products in which the improvements of the present invention are embodied, the principles and procedures of operation set forth in my above-mentioned copending application advantageously are followed in order to insure controlled production of chromate products having predetermined chemical composition and physical properties, except, of course, that a nitrate anolyte is employed in place of the acetate or chlorate anolyte referred to in the said application. The nitrate anolyte preferably is an aqueous solution containing between 2 and 8% by weight of sodium nitrate or other alkali metal (including ammonium) nitrate. The nitrate concentration preferably is not less than about 2% by weight of the anolyte, for at lower concentrations the cell voltage increases to uneconomic values, while a concentration of nitrate in excess of about 8% by weight of the anolyte leads to uneconomic nitrate consumption without beneficially lowering the cell voltage. An anolyte containing about 4% by weight of sodium nitrate or other alkali metal nitrate is particularly satisfactory.

Depending on the type of chromate product desired to be produced, the anolyte also contains small percentages of hydroxyl ions together with chromate ions (when a basic chromate product is sought), or chromate ions and dichromate ions, or only dichromate ions (when normal chromate products are desired). A typical analysis of an anolyte employed in preparing a basic lead chromate product may show the following ingredients:

	Per cent by weight
Sodium nitrate	4.0
Sodium hydroxide	0.04 to 0.06
Sodium chromate	0.02 to 0.10

As pointed out in my aforementioned application, proper control of the cell product is achieved by controlling the concentrations of hydroxyl ions, chromate ions, and dichromate ions in the electrolytes, particularly in the anolyte. The pH of the anolyte provides a convenient indication of these ion concentrations, and depending upon the pH of the anolyte different products may be formed, substantially as indicated in the following tabulation:

Anolyte pH	Ions present	Product	Color of product
7.5 to 9.5.....	Hydroxyl and chromate.	Basic lead chromate.	Orange to red orange.
6.0 to 7.5.....	Chromate and dichromate.	Normal lead chromate.	Medium yellow to medium orange.
Below 6.0.....	Dichromate.	do.....	Yellow to pale yellow.

In order to maintain the ion concentrations within proper values for the production of the desired product, the control features and procedures described in my aforementioned application may be followed.

The catholyte employed in a process embodying the present invention may be made up as described in my aforementioned application. The catholyte preferably comprises an aqueous solution containing about 2.0 to 6.0% by weight of sodium chromate, together with a small percent-

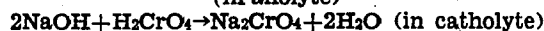
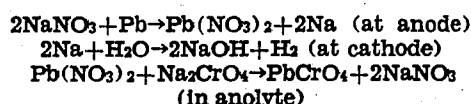
age of sodium hydroxide (when preparing basic chromates), or together with sodium dichromate (when preparing normal chromate products). When preparing certain normal chromate products, the catholyte may be free of chromate ions and contain only a suitable percentage of dichromate ions. (In the claims, the term "chromate ions" is used in referring to solutions containing either chromate or dichromate ions.)

The product of a process embodying the present invention is influenced by the temperature at which the process is carried out. For example, when producing basic lead chromates, it has been found desirable to maintain the temperature of the cell above about 50° C. In producing the normal chromates a temperature of 25° C. or less is preferable. An elevated temperature results in formation of a product of deeper (more orange or red) color than is produced at ordinary temperatures.

The current density advantageously is maintained at about 15 to 30 amperes per square foot of cathode surface, and the cell voltage advantageously is maintained at about 3.2 to 3.7 volts and operating at about 25° C. and between about 2.1 to 2.5 volts when operating at a temperature of about 50° C.

During the course of the electrolysis, the sodium nitrate present in the anolyte reacts with the lead of the anode to form lead nitrate and liberate sodium ions. The sodium ions migrate to the cathode where they combine with water to form sodium hydroxide and liberate hydrogen.

Simultaneously an equivalent amount of chromate ions are liberated at the cathode and migrate toward the anode. The chromate ions migrating into the anolyte react with the lead nitrate formed therein to produce lead chromate and to regenerate sodium nitrate. The increase in free hydroxyl ions in the catholyte resulting from these reactions is compensated for by the addition to the catholyte of chromic acid or chromic anhydride. The following equations are illustrative of the chemical reactions taking place in the production of a normal lead chromate product.



The only reagents actually consumed in the process are lead from the anode and chromic acid (or anhydride) which is added to the catholyte. The sodium nitrate is wholly regenerated, but minor losses thereof due to spillage, leakage and other mechanical causes are made up by periodically adding small amounts of sodium nitrate to the anolyte.

I claim:

1. In a method for producing lead chromates electrolytically involving passing an electric current from a soluble lead anode through an anolyte, a diaphragm, and a catholyte containing chromate ions to a cathode, the improvement which comprises employing as the anolyte an aqueous solution having dissolved therein between 2 and 8% by weight of an alkali metal nitrate and further employing a cathode current density of about 15 to 30 amperes per square foot.

2. In a method for producing lead chromates electrolytically involving passing an electric current from a soluble lead anode through an anolyte, a diaphragm, and a catholyte contain-

ing chromate ions to a cathode, the improvement which comprises employing as the anolyte an aqueous solution having dissolved therein about 4% by weight of an alkali metal nitrate and further employing a cathode current density of about 15 to 30 amperes per square foot.

3. In a method for producing lead chromates electrolytically involving passing an electric current from a soluble lead anode through an anolyte, a diaphragm, and a catholyte containing chromate ions to a cathode, the improvement which comprises employing as the anolyte an aqueous solution having dissolved therein about 2 to 8% by weight of sodium nitrate and further

employing a cathode current density of about 15 to 30 amperes per square foot.

4. In a method for producing lead chromates electrolytically involving passing an electric current from a soluble lead anode through an anolyte, a diaphragm, and a catholyte containing chromate ions to a cathode, the improvement which comprises employing as the anolyte an aqueous solution having dissolved therein about 4% by weight of sodium nitrate and further employing a cathode current density of about 15 to 30 amperes per square foot.

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